

Docket No.: 0315-0158PUS1  
(PATENT)

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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In re Patent Application of:  
Antonio Luiz Duarte BRAGANÇA et al.

Application No.: 10/518,443.

Confirmation No.: 7833

Filed: July 1, 2005

Art Unit: 1755

For: SOLID CATALYST COMPONENT FOR  
POLYMERIZATION AND  
COPOLYMERIZATION OF ETHYLENE,  
AND, PROCESS FOR OBTAINING THE  
SAME

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Examiner: J. E. McDonough

**DECLARATION UNDER 37 C.F.R. 1.132**

MS AMENDMENT  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

1. I, Dr. Marcia S. Lacerda Miranda, do declare that I am a graduate of Universidade Estadual Paulista with a Doctorate degree (Ph.D.) in inorganic chemistry. In the course of my education and training I have developed an expertise in a number of technical areas, including Nuclear Magnetic Resonance Spectroscopy (NMR) for organic compounds; polymers and organometallic compounds; viscosity analysis of polymers; organic synthesis, asymmetric synthesis, heterogeneization of organometallic compounds; development of new routes of synthesis of Ziegler-Natta catalysts; bench scale olefin polymerization, and the like.

2. I have been employed by Brasken S.A. of Brazil, the assignee of the present application for ten (10) years. During this time I have worked as a research chemist involving the synthesis of metallocene and Ziegler-Natta catalysts in the organic and organometallic synthesis for polymerization.

I have been an author and/or co-author of a number of scientific publications, including "Copolymerization of Ethylene and 1-octane: Correlation between type of Catalyst and Comonomer Incorporated and "Synthesis and "Characterization of Ethylene-1-Hexene Copolymers using Homogenous Ziegler-Natta Catalysts."

3. My present primary responsibility with Braskem is to coordinate the prosecution of the above-identified application, worldwide and to facilitate the marketing of the subject matter of the instant application worldwide.

4. An interview was conducted with the Examiner, James McDonough, Ph.D. and his supervisor, Jr. Jerry Lorengo. During the interview it was pointed out by the Applicants that the present invention defines a unique catalyst composition which contains specific amounts of catalytic active components which when used in a polymerization process produces homopolymers and/or copolymers of either high density polyethylene (HDPE) or linear low density polyethylene (LLDPE) with a controlled morphology, having one or more of the following properties, i.e., high bulk density, a very small quantity of fines in the product, good co-monomer insertion, improved catalytic activity with low catalytic decay, and a substantial

homogenous distribution of the alpha-olefin within the polymer chain in connection with LLDPE.

The Examiner's concern raised in the interview was the Applicants' ability to show a "nexus" between the Applicants' specific catalyst composition and the product produced by the use of the Applicants' catalyst composition, said product having the advantageous properties referred to hereinabove. Although it is believed that the Applicants have made such a showing by way of Examples and Comparative data provided in the original application as well as during the prosecution of the present application, the Applicants are resubmitting all of the Applicants' documentation and presenting this evidence of patentability in the present Declaration for consideration by the Examiner.

The catalyst system of the present invention contains three important elements, i.e., Titanium, Magnesium and Chlorine. Table I (below) compares the amount of these elements with that of Luciani I, Luciani II and Neste, which represent the prior art relied upon by the Examiner.

TABLE 1 – Elemental ranges

	Present Application	EP 0480435 B1 Luciani I	EP0522651 B1 Luciani II	WO91/08239 Neste
Ti range (% w/w)	0.5 - 2.0	3.9 - 4.5 (outside)	3.7 - 4.4 (outside)	3.2 - 4.9 (outside)
Mg range (% w/w)	0.3 - 3.0	2.7 - 5.0 (outside)	3.4 - 3.9 (outside)	0.70 - 1.75 (inside)
Cl range (% w/w)	5.0 - 12.0	17.7 - 21.0 (outside)	12.4 - 19.7 (outside)	12.2 - 22.5 (outside)
TOTAL (% w/w)	5.8 - 17.0	24.3 - 30.5 (outside)	19.5 - 28.0 (outside)	16.1 - 29.15 (barely inside)

Table 1 clearly shows that in Luciani I, Ti at the lower end of the range, "3.9", falls outside of the Applicants' upper limit of its range "2" by an amount of at least about 100%. The lower end of Luciani I's Mg range, "2.7" barely falls within the Applicants' upper limit range "3.0," however, Cl at its lower end of its range, "17.7," falls outside of the Applicants' upper limit of its range "12," by an amount of about 50%.

Table 1 also shows that in Luciani II, Ti, Mg and Cl all fall outside of the Applicants' ranges.

Table 1 further shows that in Neste Ti and Cl fall outside of Applicants' ranges while Mg falls within the Applicants' range.

Also, comparing total amounts of Ti, Mg and Cl, of the present invention with the prior art it can be seen that Luciani I and II falls completely outside of the Applicants' ranges whereas Neste barely overlaps with the upper limit of the Applicants' range.

The important aspect regarding the elemental ranges (Table 1) is that in Luciani I, Luciani II and Neste, the Ti amount is very high and to activate these sites it is usual to use a high amount of the cocatalyst which is usually an aluminum alkyl. This aluminum alkyl acts, in this case, as a Lewis acid and can remove from Ti and also from Mg sites, any donor or electron donor compound, beyond its function as reducing and alkylating agent. In both Luciani I and Luciani II patents they use a donor or electron donor as a solvent for the titanium and magnesium solution. The remaining donor at the final catalyst can be removed by this aluminum alkyl, during the polymerization. One of the reasons to use a donor, as mentioned before, is to obtain homogeneity on titanium sites and, consequently, obtain fewer sites which produce the xylene soluble fraction in LLDPE. Consequently, when the catalyst has a high amount of titanium sites,

the comonomer response is not as good as that of the present invention which uses a catalyst with a very small amount of titanium.

Table 2 below demonstrates a comparison between examples from Luciani I, Luciani II and Neste and an example of the catalyst of the present invention, used in copolymerization of ethylene and butene-1 to produce a LLDPE product. The examples from Luciani I, Luciani II and Neste were reproduced in the lab and used in copolymerization, as shown in Table 2.

Table 2

Comparative Test Number	TEST 1	TEST 2	TEST 3	TEST 4	TEST 5	TEST 6	TEST 7	TEST 8
Product	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE	LLDPE
Catalyst from	EP 0522651 B1 patent (Example 1)	EP 0522651 B1 patent (Example 4)	EP 0480435 B1 patent (Example 3)	EP 0522651 B1 patent (Example 1)	WO 91/08239 patent (Example 10)	WO 91/08239 patent (Example 10)	WO 91/08239 patent (Example 10)	Patent Application - 0315-0158PUS1 (Example 8)
Ti (%w/w)	6.8	5.2	5.6	6.8	3.9	3.9	3.9	2.0
Mg (%w/w)	2.7	3.4	2.3	2.7	1.9	1.9	1.9	1.5
Aluminum:alkyl	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL	TEAL
Ethylene partial pressure (bar)	5	5	5	5	5	5	5	5
Temperature (°C)	75	75	75	75	75	75	75	75
Time (h)	3	3	3	3	3	3	3	3
Al/Ti	300	300	300	300	300	300	300	300
Butene-1 (L)	0.29	0.29	0.29	0.7	0.29	0.7	1.1	0.29
H <sub>2</sub> /C <sub>2</sub> molar ratio	0.47	0.47	0.40	0.40	0.47	0.40	0.35	0.40
Bulk Density (g/cm <sup>3</sup> )	0.26	0.30	0.27	0.29	0.30	0.31	N.A.	0.36
Fines (%)	N.A.	3.0	2.8	2.2	1.5	1.7	N.A.	0.1
MFI (2,16) (g/10')	1.00	1.30	0.40	1.34	0.29	1.25	1.30	0.91
Butene content (% w/w)	5.7	6.7	4.7	9.7	5.5	N.A.	N.A.	8.7
Density (g/cm <sup>3</sup> )	0.938	0.925	0.928	0.918	0.925	0.923	N.A.	0.917
Xylene soluble (% w/w)	5.3	7.3	6.9	14.2	3.0	5.2	N.A.	9.7

N.A. = not analyzed

The copolymerization condition to specify a LLDPE product, with MIE close to 0.8 - 1.3 g/10 min range and a density close to 0.9170-0.9190 g/cm<sup>3</sup>, for catalyst Example 8 of the present invention is demonstrated in Test 7 of Table 2 (see the description of polymerization conditions on Example 12 of the present application). It can be seen in Table 2, that this copolymerization condition was the same for all Tests with the exception of Tests 4 and 6, where a higher amount of butene-1 was used (0.70 L). It can be seen from Table 2 that, using the same conditions of Test 7, from the present application, neither catalysts from Test 1, 2, 3 nor 5 showed a LLDPE product with a Density close to that obtained in Test 7. To obtain the same range of MIE of LLDPE obtained in Test 7, it was necessary to have a higher H<sub>2</sub>/C<sub>2</sub>= molar ratio for Tests 1, 2 and 5. To obtain a LLDPE product with a density closer to that shown in the Test 7, it was necessary to use higher amounts of butene-1 during the copolymerization, as can be seen in Test 4. For the catalyst example from Neste, it was not possible to obtain a density between 0.9170-0.9190 g/cm<sup>3</sup>, with the amount of 0.70 L of butene-1, as can be seen in Test 6.

In all of these products the xylene soluble fraction was analyzed. When the same kind of product is compared for Tests 4 and 7 (LLDPE with the same MIE and Density ranges), it can be seen that the xylene soluble fraction is quite different (14.2 and 9.7 % w/w, respectively). These different xylene soluble fraction results are due to the following facts:

1- The prior art (Luciani I, Luciani II and Neste) uses a high amount of Titanium: to activate these sites it is usual to use a high amount of the cocatalyst which is usually an aluminum alkyl. This aluminum alkyl acts, in this case, as a Lewis acid and can remove from Ti

sites (and also from Mg sites), any donor or electron donor compound. Thus, in Luciani I and Luciani II an electron donor is used as a solvent for the titanium and magnesium solution.

2 - The present invention uses a low amount of Ti and Mg. The smaller xylene soluble fraction is due to the lower amount of the titanium and magnesium relative to the silica support and the ratio between titanium and magnesium compounds used.

Table 2 clearly shows that by utilizing the catalyst system of the present invention a LLDPE product of high bulk density (0.36 – a minimum 16+% improvement over the closest prior art) at a sufficiently low polymer density (0.917) and with a reduced amount of fines can be effectively achieved.

As the Examiner will appreciate, catalyst systems are sensitive to many influences and as such are unpredictable in their behavior. This is clearly shown in the Experimental Data presented in Table 2, when arguably small changes in the catalyst composition produces results such as a high bulk density, a small amount of fines and low amount of xylene solubles, all of which drastically influence economic considerations. The economic importance of the present application can be understood by the research and development costs already invested as well as the high level of interest generated with BASF and W.R. Grace as shown in the Declaration of Commercial Success submitted herewith.

Additional examples showing many of the advantageous features of the present invention can be found in Examples 13 to 23 of the present application as summarized in Table 1 on page 31. The polymers produced in Examples 13 to 23 utilized the catalysts produced in Examples 1 to 10. In all examples a good catalytic yield and no agglomerates on sheets were formed. The polymer obtained possessed good morphology and in most cases, less than 1% of fines (<250

μm). Also, the films obtained with these polymers presented good optical properties and low blocking strength.

In order to further demonstrate the technical effects of the present invention over Luciani I, the Applicants present here-in-below the results of the test conducted to compare the properties of polymers obtained by polymerization or copolymerization processes using catalysts prepared according to Luciani I and the present invention.

The tests described here-in-below were carried out using exactly the same polymerization conditions employed in the examples of Luciani I, but using different catalytic systems, i.e., catalyst according to Example 1 of Luciani I or catalyst according to Examples 11 or 12 of the present application.



Table 3

Comparative Test Number	1	2
Product	HDPE	HDPE
Catalyst used	Ex.1 of Luciani I	Ex. 11 of the present application
Alkyl-aluminum	TEAL	TEAL
Catalyst mass (mg)	60	60
Temperature (°C)	90	90
Time (h)	2	2
Al/Ti	70	70
H <sub>2</sub> /C <sub>2</sub>	0.47	0.47

Activity (KgPol/gTi)	4.2	3.0
Bulk Density (g/cm <sup>3</sup> )	0.32	0.40
MIF (2,16) (g/10min)	2.84	0.9
Density (g/cm <sup>3</sup> )	0.9563	0.9632

Comparative Test Number	3	4
Product	LLDPE	LLDPE
Catalyst used	Ex.1 of Luciani I	Ex. 12 of present application
Alkyl-aluminum	TEAL	TEAL
Catalyst mass (mg)	60	60
Temperature (°C)	75	75
Time (h)	3	3
Al/Ti	300	300
C <sub>4</sub> (ml)	290	290
H <sub>2</sub> /C <sub>2</sub>	0.40	0.40

Activity (KgPol/gTi)	3.0	6.6
Bulk Density (g/cm <sup>3</sup> )	0.26	0.36
Mesh 250 + bottom (%)	2.8	0.1
MIF (2,16) (g/10min)	0.40	0.91
Content of binded butene (%)	4.7	8.7
Density (g/cm <sup>3</sup> )	0.9283	0.9170

The above results, relative to the tests 2 and 4, show a higher bulk density, a lower amount of fines and a better comonomer insertion (test 4 only) for the polymer obtained according to the present invention.

The tests shown here-in-below (Table 4) were carried out using exactly the same polymerization condition employed in the examples of Luciani II, but using different catalytic systems: catalyst according to Ex. 1 of Luciani II (test 5), catalyst according to Ex. 4 of Luciani II (test 6) and catalyst according to Ex. 11 of the present patent application (test 7).

The results obtained in tests 5 and 6 are quite similar to the corresponding ones presented in Luciani II, which show the correctness of Applicants' proceedings.

The higher bulk density and the low quality of fines obtained in test 7 show the superiority of the polymer prepared according to the present invention. The value obtained for the bulk density ( $0.40 \text{ g/cm}^3$ ) is within the range of  $0.33\text{-}0.438 \text{ g/ml}$  considered by US 5,585,317 as distinctive of HDPE having good morphology.

Table 4

Comparative Test Number	5	6	7
Product	HDPE	HDPE	HDPE
Catalyst used	Ex.1 of Luciani II	Ex.4 of Luciani II	Ex.11 of the present application.
Alkyl-aluminum	TEAL	TEAL	TEAL
Catalyst mass (mg)	60	60	60
Temperature ( $^{\circ}\text{C}$ )	90	90	90
Time (h)	1.5	1.5	1.5
Al/Ti	50	50	50
$\text{H}_2/\text{C}_2$	0.47	0.47	0.47
Activity (KgPol/gTi)	37.0	109.0	100.0
Bulk Density ( $\text{g/cm}^3$ )	0.30	0.32	0.40

Mesh 250 + bottom (%)	-	7.12	0.17
MIF (2.16) (g/10min)	2.51	2.46	0.9
Density (g/cm <sup>3</sup> )	0.9592	0.9572	0.9632

Similarly, tests were carried out for LLDPE using different catalysts of Luciani II (tests 8 and 9) and of the catalyst of the present invention (test 10) and following the polymerization conditions employed in Example 12 of the present application, since Luciani II itself does not present any test for LLDPE

Table 5

Comparative Test Number	8	9	10	11
Product	LLDPE	LLDPE	LLDPE	LLDPE
Catalyst used	Ex.1 of Luciani II	Ex.4 of Luciani II	Ex.12 of the present application.	Ex.1 of Luciani II
Alkyl-aluminum	TEAL	TEAL	TEAL	TEAL
Catalyst mass (mg)	60	60	60	60
Temperature (°C)	75	75	75	75
Time (h)	3	3	3	3
Al/Ti	300	300	300	300
C <sub>4</sub> <sup>+</sup> (ml)	290	290	290	700
H <sub>2</sub> /C <sub>2</sub> <sup>+</sup>	0.47	0.47	0.47	0.40
Activity (KgPol/gTi)	74	300	330	76
Bulk Density (g/cm <sup>3</sup> )	0.26	0.30	0.36	0.28
Mesh 250 + bottom (%)	-	3.0	0.1	0.1
MIF (2.16) (g/10min)	1.00	1.30	0.91	1.34
Content of binded butene (%)	5.7	6.7	8.7	9.7
Density (g/cm <sup>3</sup> )	0.9382	0.9251	0.9170	0.9187
Xylene solubles (%)	5.3	7.3	9.7	14.2

The polymer prepared according to the present invention produces better comonomer insertion (50% more butane incorporated in test 10 comparing to the value of test 9), higher bulk density and lower amount of fines. Once again, the bulk density obtained ( $0.36 \text{ g/cm}^3$ ) is within the range provided by US 5,585,317 upon describing LLDPE with good morphology.

In the test number 11, Applicants use a catalyst in accordance with Luciani II and change the process conditions, particularly the amount of butene in the reaction medium, in order to obtain a final product having a density very similar to that of the product of test 10, in which a catalyst according to the present invention is employed.

The butene is so badly distributed in the molecule of test 11 that the content thereof should be much higher so that the desired low density is obtained. The bad comonomer insertion also produces a higher amount of solubles, when compared to the result of test 10, in connection therewith, please note that the soluble amounts of the products obtained in tests 8 and 9 are lower than that of test 10 simply because their densities are higher than the density of the product obtained according to the present invention (test member 10).

The low amount of fines obtained in test 11 (0.1%) is due to the great quantity of solubles which leads to a sticky product in which the small particles remain joined together.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States

Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

January 8<sup>th</sup>, 2028  
Date

Marcia S. Lacerda Miranda  
Dr. Marcia S. Lacerda Miranda